Crystal Field $-AS_z^2$ Does Not Produce One-Phonon Transitions With $\Delta S_z = \pm 2$ [Comment on EPL 46, 692 (1999) by Leuenberger and Loss]

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Recently Leuenbeger and Loss suggested a theory of phonon-assisted relaxation in a molecular nanomagnet Mn-12 that "contrary to previous results is in reasonably good agreement not only with the relaxation data but also with all experimental parameter values known so far" [1, 2]. The purpose of this Comment is to show that the model of Leuenberger and Loss and its comparison with experiment are premised upon a principal error.

The theory of Ref. [1] follows the footsteps of our earlier work [3] that describes phonon-assisted magnetic relaxation in Mn-12 in terms of the master equation for the density matrix. The dominant term in the crystal field of Mn-12 is $-AS_z^2$. Performing rotation of the anisotropy axis due to the elastic deformation **u**, one obtains the following magnetoelastic coupling [3]

$$A(\omega_{xz}\{S_x, S_z\} + \omega_{yz}\{S_y, S_z\}) = (A/2)[(\omega_{xz} - i\omega_{yz})\{S_+, S_z\} + (\omega_{xz} + i\omega_{yz})\{S_-, S_z\}] \ , \quad (1)$$

where $\omega_{\alpha\beta} = \frac{1}{2}(\partial_\beta u_\alpha - \partial_\alpha u_\beta)$. Operators $S_\pm$ change the S_z projection of spin by ± 1, while **u** is linear on the operators of creation and annihilation of phonons. Consequently, Eq. (1), when quantized, describes emission and absorption of one phonon accompanied by $\Delta S_z = \pm 1$.

According to Leuenberger and Loss [1, 2], the crystal field $-AS_z^2$ also produces the magnetoelastic coupling of the form

$$A(\epsilon_{xx} - \epsilon_{yy})(S_x^2 - S_y^2) = (A/2)(\epsilon_{xx} - \epsilon_{yy})(S_+^2 + S_-^2) \ . \quad (2)$$

where $\epsilon_{\alpha\beta}$ is the strain tensor. This coupling generates "second-order" spin-phonon transitions with $\Delta S_z = \pm 2$, which "lead to a much faster relaxation of the spin system" than "first-order" transitions with $\Delta S_z = \pm 1$.

The error stems from the use by Leuenberger and Loss [1, 2] of the linear formula for the strain rensor,

$$\epsilon_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha}\right) \ , \quad (3)$$

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instead of the exact expression [4],

$$\epsilon_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} + \frac{\partial u_\gamma}{\partial x_\alpha}\frac{\partial u_\gamma}{\partial x_\beta}\right) \quad . \tag{4}$$

To obtain Eq. (2) Leuenberger and Loss computed the rotation matrix $\hat{R}$ and the corresponding deformation, $\mathbf{u} = (\hat{R}_z\hat{R}_y\hat{R}_x - 1)\mathbf{x}$, up to the *second order* in infinitesimal rotation $\delta\phi_\alpha$. They obtained [1, 2]

$$\begin{aligned} u_x &= \delta\phi_y z - \delta\phi_z y - (1/2)(\delta\phi_y^2 + \delta\phi_z^2)x \\ u_y &= \delta\phi_z x - \delta\phi_x z - (1/2)(\delta\phi_x^2 + \delta\phi_z^2)y \\ u_z &= \delta\phi_x y - \delta\phi_y x - (1/2)(\delta\phi_x^2 + \delta\phi_y^2)z \end{aligned} \tag{5}$$

The incorrect Eq. (3) then gives (incorrectly)

$$\epsilon_{xx} = -(\delta\phi_y^2 + \delta\phi_z^2)/2, \qquad \epsilon_{yy} = -(\delta\phi_x^2 + \delta\phi_z^2)/2, \qquad \epsilon_{zz} = -(\delta\phi_x^2 + \delta\phi_y^2)/2, \tag{6}$$

and one gets $\delta\phi_x^2 = \epsilon_{xx} - \epsilon_{yy} - \epsilon_{zz}$ and cyclic permutations for $\delta\phi_y^2$ and $\delta\phi_z^2$. Substituting this into $\hat{R}$ and inserting the rotated spin vector $R_x R_y \mathbf{S}$ into $-AS_z^2$, Leuenberger and Loss obtained Eq. (2). One should notice, however, that the substitution of Eq. (5) into the correct expression for the strain tensor, Eq. (4), yields

$$\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz} = 0 \quad , \tag{7}$$

in accordance with the fact that rotation does not change the volume, $\delta V = V\sum \epsilon_{\alpha\alpha} = 0$.

In fact, to see that Eq. (2) cannot be right no calculation is needed. Indeed, the operator $-AS_z^2$ conserves S_z. In order to change the magnetic quantum number of Mn-12 molecule by 2, one would have to assign to phonons spin 2. Phonons, however, being described by a vector field $\mathbf{u}$, cannot possess spin other than 1 [5]. One-phonon processes accompanied by $\Delta S_z = \pm 2$ can only be generated by terms in the crystal field which do not conserve S_z. For Mn-12 these are tunneling terms which are orders of magnitude smaller than the uniaxial crystal field. Leuenberger and Loss (see Appendix D of Ref. [2]) find support of their incorrect statement on p. 563 of Abragam and Bleaney [6]. However, Abragam and Bleaney, when talking about "first-" and "second-order" transitions, mean two-phonon Raman processes, which, of course, are not prohibited by the above argument. These two-phonon processes die out at low temperature. Their rate is inversely proportional to the tenth power of the sound velocity, as compared to the fifth power for the one-phonon processes. Leuenberger and Loss compare their theory with experiment based upon the extraction of the sound velocity from the measured relaxation rate, using a wrong type of the phonon process. Their claim of agreement with experiment is, therefore, completely invalidated by their incorrect model for the spin-phonon coupling.

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